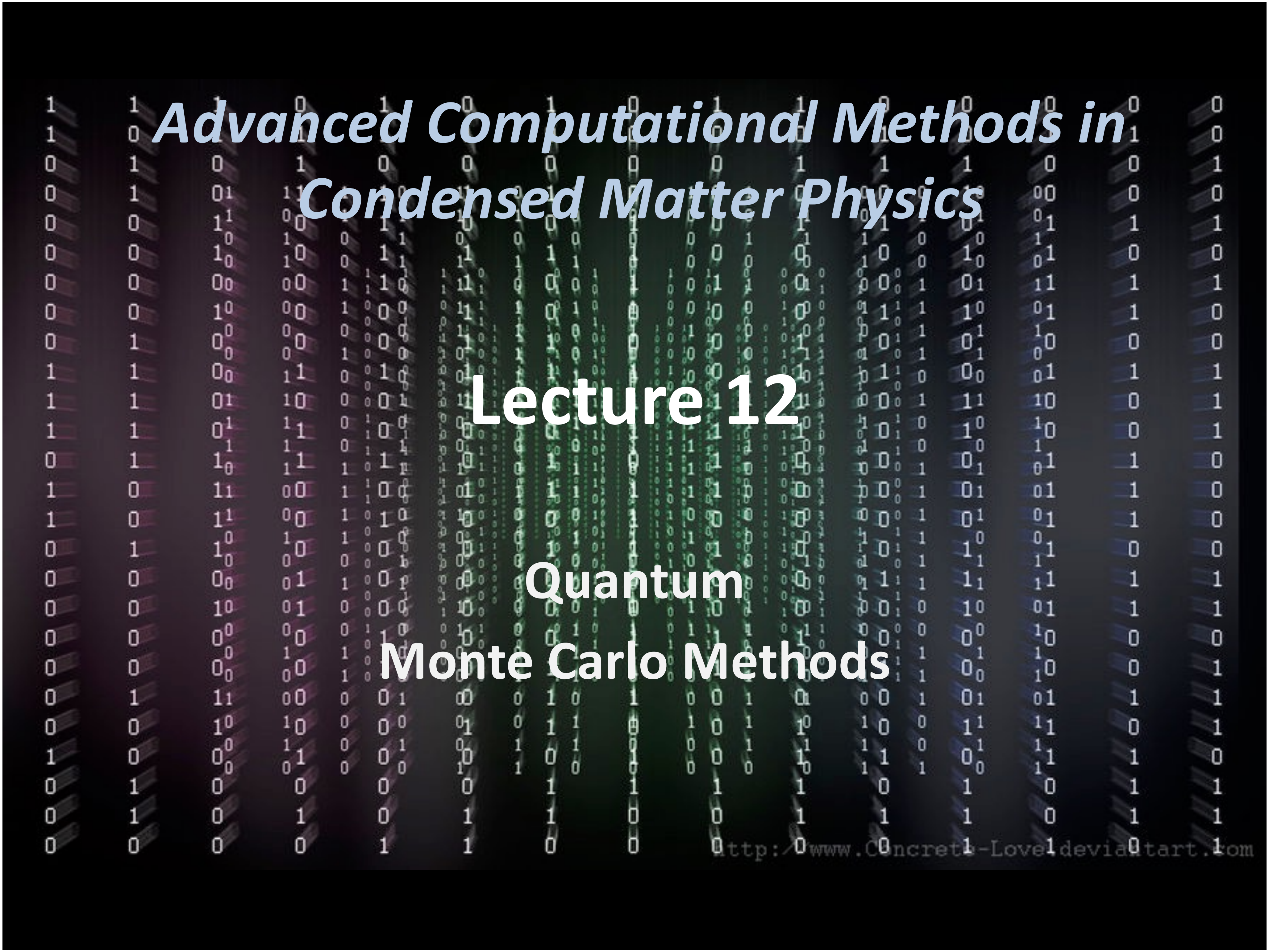

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Advanced Computational Methods in Condensed Matter Physics

Lecture 12

Quantum Monte Carlo Methods

Motivation

Quantum mechanical simulations

- Density functional theory methods
  Large systems but approximate exchange/correlation
- Quantum chemistry post-Hartree-Fock methods
  Accurate on small-medium systems
  → Jungle of approaches: CI, MCSCF, CC, CASPT2...

- **Quantum Monte Carlo techniques**
  Stochastic solution of the Schrödinger equation
  Accurate correlated calculations for medium-large systems

What is Quantum Monte Carlo (QMC)?

- Aims at studying complex quantum systems
  → *reliable solution (or an accurate approximation) of the quantum many-body problem:*

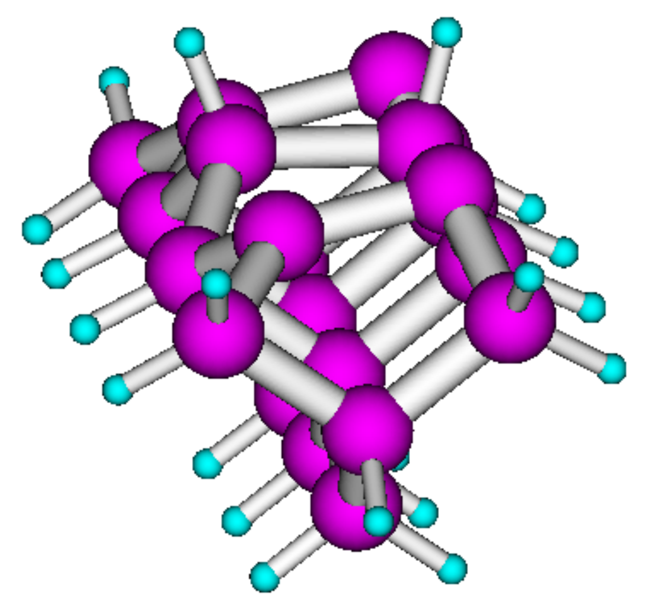
$$\hat{\mathcal{H}}\psi = E\psi$$

(relativistic effects neglected - ok for most CM applications)

- Involves computation of high-dimensional integrals
- Direct solution impossible since wave function /Hilbert space exponentially large in particle number
- Solution can be better than mean-field or Hartree–Fock approximations
- Solution typically better for Bosons than for Fermions

Example

$Si_{21}H_{22}$



Number of electrons: $4 \times 21 + 22 = 106$
Number of dimensions: $3 \times 106 = 318$

Integral on a grid with 10 points/dimension
$\rightarrow 10^{318}$ points!

MC is a powerful "trick" ⇒ Freedom in form of the wave function Ψ

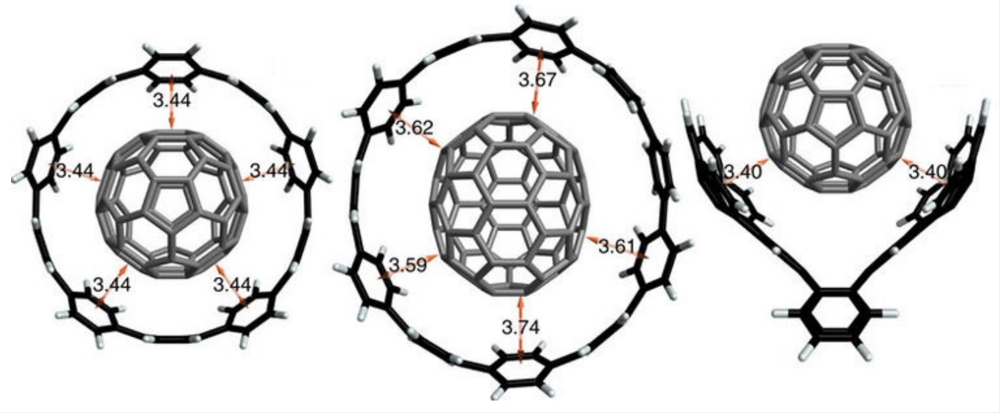
QMC

Stochastically solve interacting Schrödinger equation

Why (real-space) quantum Monte Carlo?

- Favorable scaling → Energy is O(N^4)
- Flexibility in choice of functional form of wave function
- Easy parallelization
- Among most accurate calculations for medium-large systems

Routinely, molecules of up to 100 (mainly 1st/2nd-row) atoms



Up to $C_{136}H_{44}$ (Alfe 2017)

Typical QMC methods

Zero-temperature (only ground state)

- **Variational Monte Carlo**: commonly used in many quantum problems
    - **Diffusion Monte Carlo**: most common high-accuracy method for electrons (i.e., chemical problems), since it comes quite close to the exact ground-state energy fairly efficiently. Also used for simulating the quantum behavior of atoms, etc.
    - **Reptation Monte Carlo**: Recent zero-temperature method related to path integral Monte Carlo, with applications like diffusion Monte Carlo
- **Gaussian quantum Monte Carlo:** uses density matrix in Gaussian basis with positive coefficients to avoid Fermion sign problem
- **Path integral ground state**: Mainly used for boson systems; for those it allows calculation of physical observables exactly, i.e. with arbitrary accuracy

…

Finite-temperature (thermodynamic)

- **Auxiliary-field Monte Carlo**: Usually applied to lattice problems; recently also applied to electrons in chemical systems
- **Continuous-time quantum Monte Carlo**
- **Determinant quantum Monte Carlo** or **Hirsch–Fye quantum Monte Carlo**
- **Hybrid quantum Monte Carlo**
- **Path integral Monte Carlo**: Finite-temperature technique mostly applied to bosons where temperature is very important, especially superfluid helium.
- **Stochastic Green function algorithm**: An algorithm designed for bosons that can simulate any complicated lattice Hamiltonian that does not have a sign problem.
- **World-line quantum Monte Carlo**
- **Stochastic series expansion**, a method which avoids the discretization error associated with path integral Monte Carlo by approximating the Taylor series expansion of the partition function using Monte Carlo sampling

…

Real-time dynamics (closed quantum systems)

- **Time-dependent variational Monte Carlo**: extension of the variational Monte Carlo to study dynamics of pure quantum states

Why QMC? Examples

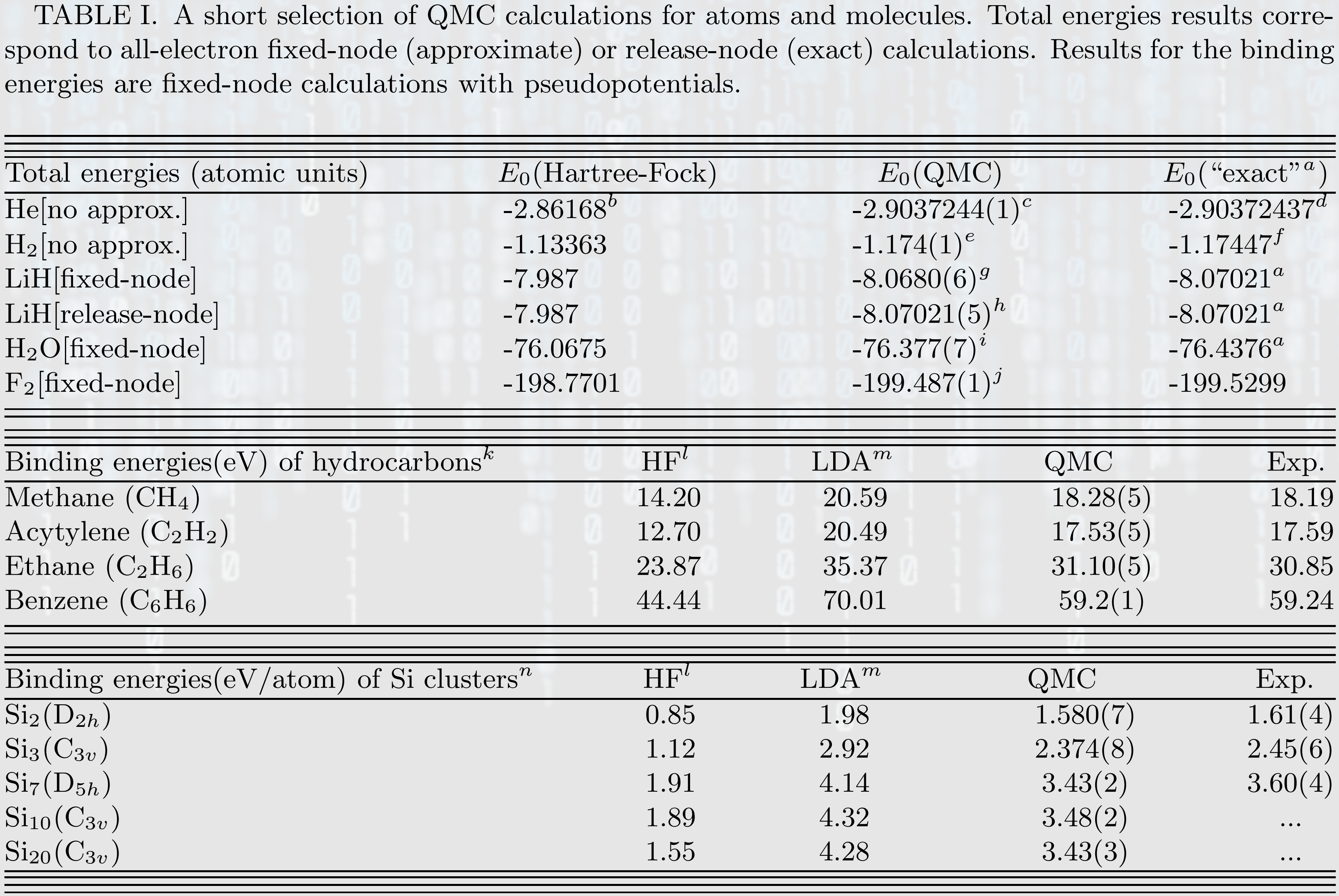


TABLE I. A short selection of QMC calculations for atoms and molecules. Total energies results correspond to all-electron fixed-node (approximate) or release-node (exact) calculations. Results for the binding energies are fixed-node calculations with pseudopotentials.

Total energies (atomic units)	E_0(Hartree-Fock)	E_0(QMC)	E_0("exact"^{a})
He[no approx.]	-2.86168^b	$-2.9037244(1)^c$	-2.90372437^d
H_2[no approx.]	-1.13363	$-1.174(1)^e$	-1.17447^f
LiH[fixed-node]	-7.987	$-8.0680(6)^g$	-8.07021^a
LiH[release-node]	-7.987	$-8.07021(5)^h$	-8.07021^a
H_2O[fixed-node]	-76.0675	$-76.377(7)^i$	-76.4376^a
F_2[fixed-node]	-198.7701	$-199.487(1)^j$	-199.5299

Binding energies(eV) of hydrocarbons^k	HF^l	LDA^m	QMC	Exp.
Methane (CH_4)	14.20	20.59	18.28(5)	18.19
Acytylene (C_2H_2)	12.70	20.49	17.53(5)	17.59
Ethane (C_2H_6)	23.87	35.37	31.10(5)	30.85
Benzene (C_6H_6)	44.44	70.01	59.2(1)	59.24

Binding energies(eV/atom) of Si clusters^n	HF^l	LDA^m	QMC	Exp.
$Si_2(D_{2h})$	0.85	1.98	1.580(7)	1.61(4)
$Si_3(C_{3v})$	1.12	2.92	2.374(8)	2.45(6)
$Si_7(D_{5h})$	1.91	4.14	3.43(2)	3.60(4)
$Si_{10}(C_{3v})$	1.89	4.32	3.48(2)	...
$Si_{20}(C_{3v})$	1.55	4.28	3.43(3)	...

From: *A pedagogical introduction to quantum Monte Carlo* by Michel Caffarel and Roland Assaraf

The Sign Problem

E. Y. Loh, J. E. Gubernatis, R. T. Scalettar, S. R. White, D. J. Scalapino, and R. L. Sugar. *Sign problem in the numerical simulation of many-electron systems*. Phys. Rev. B **41**, 9301 (1990)
Or see: arXiv:2204.08777v2 (2022)

In QMC simulation, the partition function of the interacting problem is cast into a sum (or integral) over configurations in a chosen basis → cover the exponentially large configurational space in polynomial time

But: oscillating positive and negative (or even complex) weights can occur in the simulations → **statistical errors to grow exponentially with particle number and inverse temperature**, especially in Fermion systems (fully anti-symmetric wave functions)

probability sampling → "quasi-probability" sampling

simulation must separate these positive and negative parts or try to avoid the problem, e.g., by using Gaussian quantum Monte Carlo (this causes typically other issues).

Fermions

Fermions → Ψ is antisymmetric and changes sign!

- All fermion QMC methods suffer from sign problems
- These sign problems look different but have the same “flavor”
- Arise when you treat something non-positive as probability density

For DMC (later) one can evolve separate positive and negative populations of walkers:

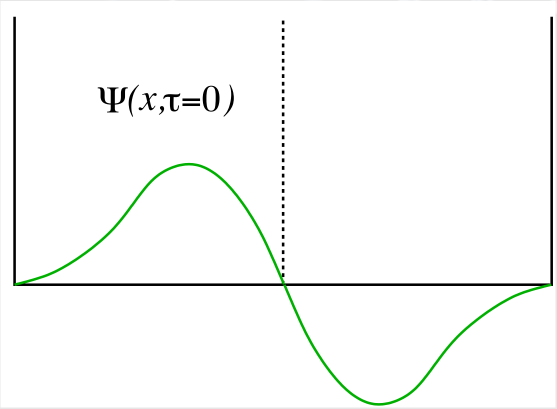
Example: 1D antisymmetric wave function $\psi(x,\tau=0)$

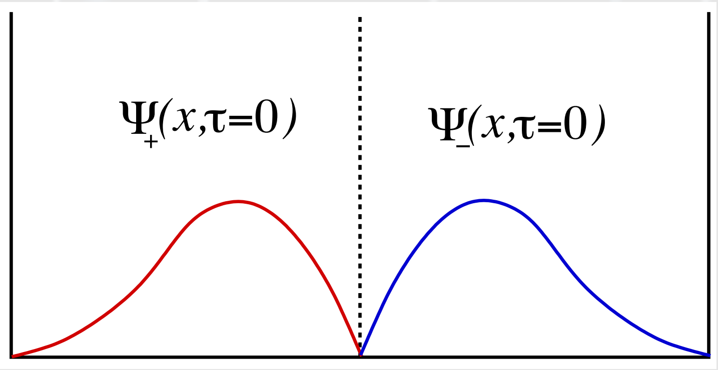
Rewrite $\Psi(x,\tau=0)$ as

$$\Psi = \Psi_+ - \Psi_-$$

with

$$\begin{aligned}\Psi_+ &= \frac{1}{2}(|\Psi| + \Psi)\\ \Psi_- &= \frac{1}{2}(|\Psi| - \Psi)\end{aligned}$$





Variational Monte Carlo (VMC)

Start with the expectation value for the energy using a generic wave function |ψ(a)>:
(*X* is a many-body configuration)

$$E(a) = \frac{\langle\Psi(a)|\mathcal{H}|\Psi(a)\rangle}{\langle\Psi(a)|\Psi(a)\rangle} = \frac{\int |\Psi(X,a)|^2 \frac{\mathcal{H}\Psi(X,a)}{\Psi(X,a)}\, dX}{\int |\Psi(X,a)|^2\, dX}.$$

The optimal value of parameters *a* is found by minimizing the energy of the system.

Interpret p(X,a)= $\dfrac{|\Psi(X,a)|^2}{\int |\Psi(X,a)|^2\, dX}$ as pdf, which is then sampled in the MC spirit

E(a) is then obtained as average of the “local energy”: $E_{\mathrm{loc}}(X) = \dfrac{\mathcal{H}\Psi(X,a)}{\Psi(X,a)}$
(using, e.g., a 3N dimensional random walk/Markov chain for X
And subsequent acceptance/rejection condition)

Finally, optimize *E(a)* as function of *a* to obtain best ground-state wave function.

VMC

Recipe:

- Use an appropriate trial wave function
- Distribute N points according to p(X,a)
- Compute the average of the local energy

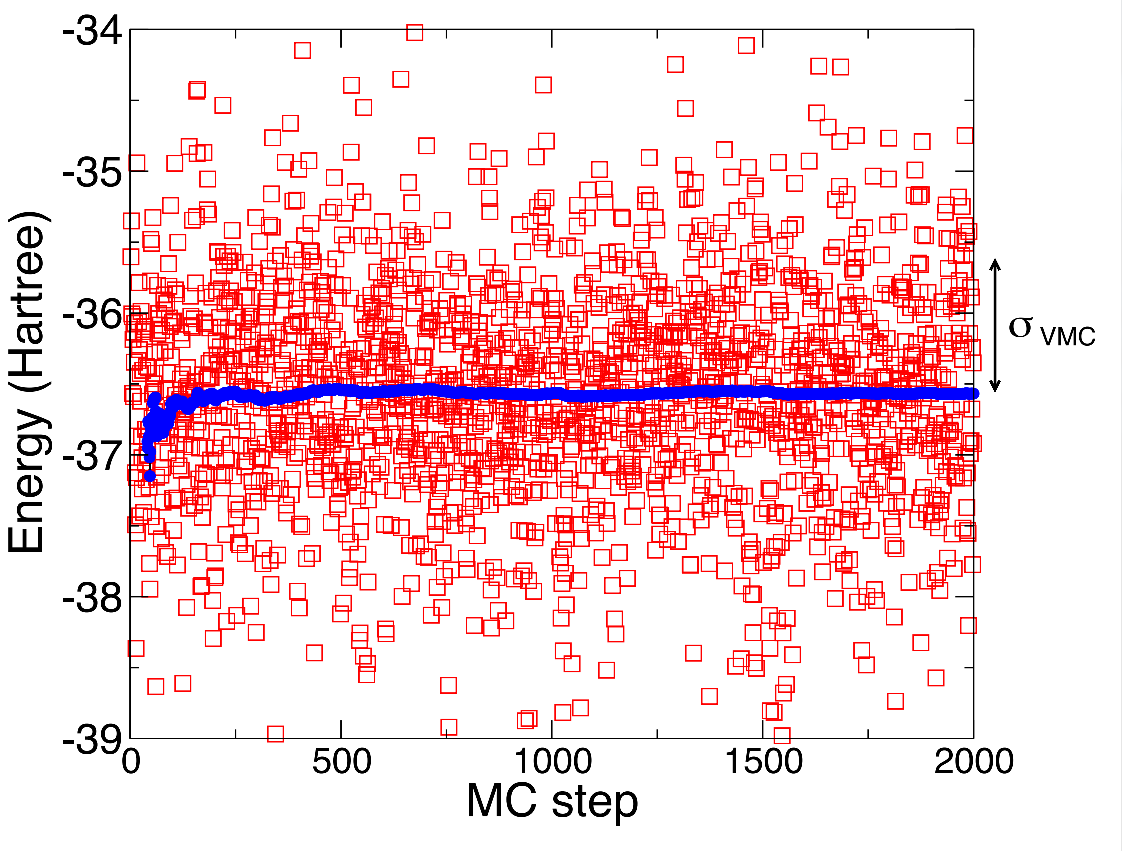
$$\sigma^2 = \frac{\langle\Psi|(\mathcal{H}-E_V)^2|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \langle (E_{\mathrm{L}}(\mathbf{R}) - E_V)^2\rangle_P$$

Remarks:

- Statistical errors are calculated as in classical MC
- accuracy of method largely depends on choice of trial state
  simple choice: product state, but no many-body effects
  better: choose approximate ground state wave function (see Jastrow factor) → ***still topic of intense research***
- *In a chemical system a 30 parameters may yield a better GS energy approximation than direct configuration interaction calculation with 50000 parameters*

Typical VMC run

Example: Local energy and average energy of acetone (C_3H_6O)



$$E_{\mathrm{VMC}} = \langle E_{\mathrm{L}}(\mathbf{R}) \rangle_P = -36.542 \pm 0.001 \text{ Hartree } (40 \times 20000 \text{ steps})$$

$$\sigma_{\mathrm{VMC}} = \langle (E_{\mathrm{L}}(\mathbf{R}) - E_{\mathrm{VMC}})^2 \rangle_P = 0.90 \text{ Hartree}$$

Advantages and Disadvantages of VMC

- Simple, easy to implement
- Intrinsic error bars
- Usually obtains 60-90% of correlation energy
- Error bar goes down as $N^{-1/2}$
- It is computationally demanding
- The optimization of ψ becomes difficult as the number of nonlinear parameters increases
- It depends critically on our skill to invent a good ψ

VMC

- VMC is a “classical” simulation method

> *Nature is not classical, dammit, and if you want to make a simulation of nature, you'd better make it quantum mechanical, and by golly it's a wonderful problem, because it doesn't look so easy.*
>
> Richard P. Feynman

- Suggested by Fermi in 1945, but implemented only in the 70’s

VMC and deep learning

- A VMC objective function can be used to train an artificial neural network to find the ground state of a quantum mechanical system.
- In general, artificial neural networks can be used as a wave function ansatz (known as neural network quantum states) in VMC frameworks for finding ground states of quantum mechanical systems.
- Can be extended to Fermions
  → enables electronic structure calculations which are significantly more accurate than VMC calculations which do not use neural networks.

Diffusion quantum Monte Carlo (DMC)

DMC can potentially be numerically exact, i.e., the exact GS energy for any quantum system can be found within a given error

DMC typically scales polynomial for Bosons, but exponentially for Fermions

- Compare classical diffusion and Schrödinger (for a free particle) equations

$$\boxed{\frac{\partial P(x,t)}{\partial t} = D\frac{\partial^2 P(x,t)}{\partial x^2}} \quad \boxed{\frac{\partial \Psi(x,t)}{\partial \tau} = \frac{\hbar^2}{2m}\frac{\partial^2 \Psi(x,t)}{\partial x^2}}$$

- Can interpret ψ as (real!) probability density with diffusion constant $D=\hbar^2/2m$ with imaginary time τ

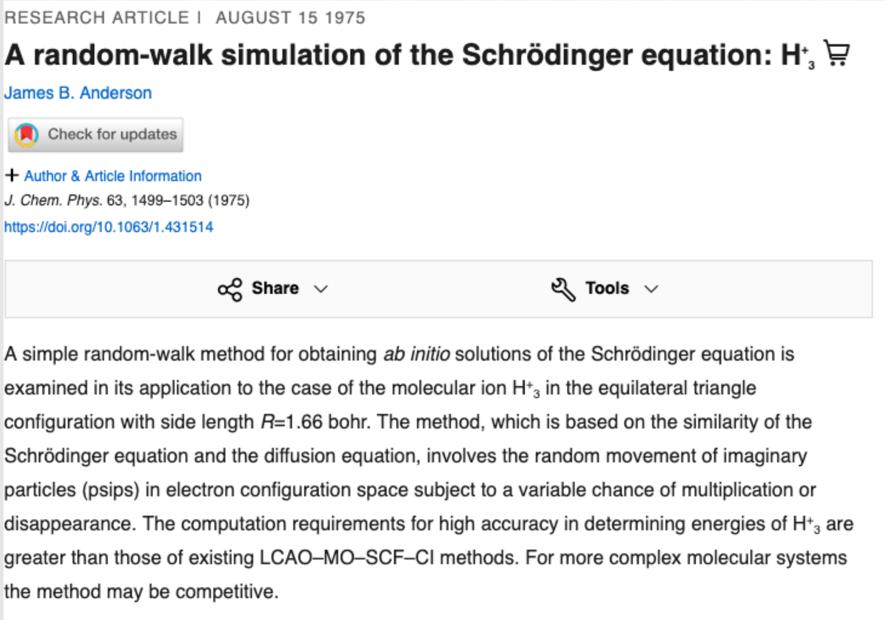
…

More general, we can study the imaginary time Schrödinger equation:

$$\frac{\partial \Psi}{\partial \tau} = D\nabla^2\Psi - V\Psi$$

where ψ can now be real and interpreted as concentration of fictious particles, called walkers

This equation then describes the process of diffusion, growth, and disappearance of walkers.



RESEARCH ARTICLE | AUGUST 15 1975

A random-walk simulation of the Schrödinger equation: H^+_3

James B. Anderson

+ Author & Article Information

J. Chem. Phys. 63, 1499–1503 (1975)

https://doi.org/10.1063/1.431514

A simple random-walk method for obtaining *ab initio* solutions of the Schrödinger equation is examined in its application to the case of the molecular ion H^+_3 in the equilateral triangle configuration with side length R=1.66 bohr. The method, which is based on the similarity of the Schrödinger equation and the diffusion equation, involves the random movement of imaginary particles (psips) in electron configuration space subject to a variable chance of multiplication or disappearance. The computation requirements for high accuracy in determining energies of H^+_3 are greater than those of existing LCAO–MO–SCF–CI methods. For more complex molecular systems the method may be competitive.

Also called Green's function Monte Carlo

Propagate imaginary time Schrödinger equation in time using a convolution integral with the Green's function:

$$\boxed{\Psi(\mathbf{R}', t+\tau) = \int \mathrm{d}\mathbf{R}\, G(\mathbf{R}', \mathbf{R}, \tau)\Psi(\mathbf{R}, t)}$$

with $G(\mathbf{R}', \mathbf{R}, \tau) = \langle \mathbf{R}' | e^{-\tau(\mathcal{H} - E_{\mathrm{ref}})} | \mathbf{R} \rangle$

- can only propagate for small time steps to be accurate
- increasing particle number → dimensionality of the integral increases (integration over all particle coordinates)
- integrate by Monte Carlo integration

Green's function

$G(\mathbf{R}', \mathbf{R}, t)$ satisfies the imaginary-time Schrödinger equation

$$\boxed{(\mathcal{H} - E_{\mathrm{ref}})G(\mathbf{R}, \mathbf{R}_0, t) = -\frac{\partial G(\mathbf{R}, \mathbf{R}_0, t)}{\partial t}}$$

with $G(\mathbf{R}', \mathbf{R}, t) = \langle \mathbf{R}' | e^{-t(\mathcal{H} - E_{\mathrm{T}})} | \mathbf{R} \rangle$ and $G(\mathbf{R}', \mathbf{R}, 0) = \delta(\mathbf{R}' - \mathbf{R})$

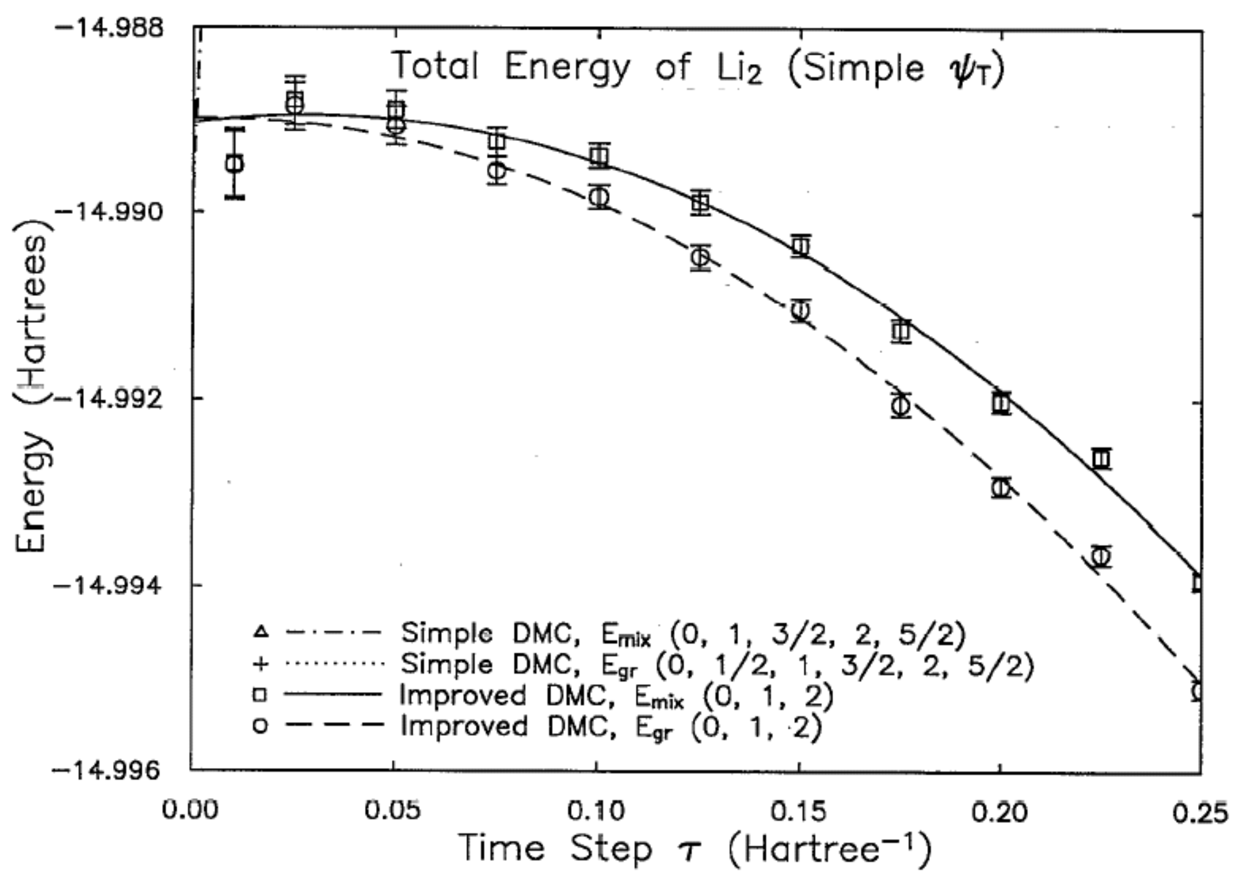
Green's function in the short-time approximation (small τ)

$$\boxed{G(\mathbf{R}', \mathbf{R}, \tau) \approx (2\pi\tau)^{-3N/2} \exp\left[-\frac{(\mathbf{R}' - \mathbf{R})^2}{2\tau}\right] \exp\left[-\tau\left(\mathcal{V}(\mathbf{R}) - E_{\mathrm{T}}\right)\right]}$$

Example

Diffusion + branching factor leading to survival/death/cloning

Time-step evolution for Li_2



Basic DMC algorithm

1. Sample $\Psi^{(0)}(\mathbf{R})$ with the Metropolis algorithm

   Generate M_0 walkers $\mathbf{R}_1, \ldots, \mathbf{R}_{M_0}$ (zeroth generation)

2. Diffuse each walker as $\boxed{\mathbf{R}' = \mathbf{R} + \xi}$

   where ξ is sampled from $g(\xi) = (2\pi\tau)^{-3N/2} \exp\left(-\xi^2/2\tau\right)$

3. For each walker, compute the factor

$$\boxed{p = \exp\left[-\tau(\mathcal{V}(\mathbf{R}) - E_{\mathrm{ref}})\right]}$$

   p is the probability to survive/proliferate/die

4. Adjust E_{ref} so that population fluctuates around target M_0

→ After many iterations, walkers distributed as $\Psi_0(\mathbf{R})$

DMC remarks

The basic algorithm is **inefficient and unstable**

- Potential can vary a lot and be unbounded
  e.g. electron-nucleus interaction → Exploding population
- Branching factor grows with system size

On solution: Introduce *Importance sampling* (multiplication by trial ψ_T)

$$\boxed{\tilde{G}(\mathbf{R}',\mathbf{R},\tau) = \Psi_\mathrm{T}(\mathbf{R}')\langle\mathbf{R}'|e^{-\tau(\mathcal{H}-E_\mathrm{ref})}|\mathbf{R}\rangle/\Psi_\mathrm{T}(\mathbf{R})}$$

Introduces a drift **V**(**R**) :

$$\boxed{-\frac{1}{2}\nabla^2\tilde{G} + \nabla\cdot[\tilde{G}\,\mathbf{V}(\mathbf{R})] + [E_\mathrm{L}(\mathbf{R}) - E_\mathrm{ref}]\,\tilde{G} = -\frac{\partial\tilde{G}}{\partial\tau}}$$

$$E_\mathrm{L}(\mathbf{R}) = \frac{\mathcal{H}\Psi_\mathrm{T}(\mathbf{R})}{\Psi_\mathrm{T}(\mathbf{R})}$$

Drift-diffusion-branching Green's function

Drift-diffusion-branching short-time Green's function

$$\tilde{G}(\mathbf{R}', \mathbf{R}, \tau) = (2\pi\tau)^{-3N/2} \exp\left[-\frac{(\mathbf{R}' - \mathbf{R} - \tau\mathbf{V}(\mathbf{R}))^2}{2\tau}\right] \times \\ \times \exp\left\{-\tau\left(E_{\mathrm{L}}(\mathbf{R}) - E_{\mathrm{ref}}\right)\right\}$$

- ➢ Drift-diffusion with **V** pushing walkers to large Ψ
- ➢ Survival/death/cloning with E_L better behaved than potential
  - Cusp conditions ⇒ No divergences when particles approach
  - As $\Psi_T \rightarrow \Psi_0$: $E_L \rightarrow E_0$ and branching factor smaller

Basic DMC algorithm with importance sampling

1. Sample initial walkers from $|\Psi_T(\mathbf{R})|^2$
2. Drift and diffuse the walkers as $\mathbf{R}' = \mathbf{R} + \tau V(\mathbf{R}) + \boldsymbol{\xi}$ where ξ is sampled from $g(\xi) = (2\pi\tau)^{-3N/2} \exp(-\xi^2/2\tau)$
3. Branching step as in the simple algorithm but with the factor $p = \exp(-\tau[(E_L(R) + E_L(R'))/2 - E_{ref}])$
4. Adjust the trial energy to keep the population stable

→ After many iterations, walkers distributed as $\Psi_T(R)\Psi_0(R)$

Other applications of quantum Monte Carlo methods

- **Electronic structure calculations**
- Strongly correlated systems (Hubbard, t-J,...)
- Quantum spin systems (Ising, Heisenberg, XY,...)
- Liquid-solid helium, liquid-solid interface, droplets
- Atomic clusters
- Nuclear structure
- Lattice gauge theory

Both zero (ground state) and finite temperature